

POLYVINYLDENE FLUORIDE MEMBRANE COATED WITH TITANIUM DIOXIDE NANOFIBERS FOR PHOTOCATALYTIC MEMBRANE PROCESS

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Special dedicated to my beloved parents

(Mohamad Nor Bin Toyib and Khadijah Binti Mat),

and my dearest family members.

I dedicated this work in sincere gratitude for your love, support and patience.

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ABSTRACT

Photocatalytic oxidation nowadays has been pledging as the valuable process for air and water purification because of its capability to degrade organic pollutants. Photodegradation of organic pollutants by suspended photocatalyst have major drawbacks in terms of difficulty in post-recovery treatment. In this study, polyvinylidene fluoride (PVDF) nanocomposite membrane consisted of electrospun titanium dioxide (TiO₂) nanofibers (PVDF/e-TiO₂) was prepared by hot pressing the as-spun TiO₂ nanofibers onto PVDF flat sheet membrane. The TiO₂ nanofibers acted as a photocatalyst, while PVDF membrane acted as a support. The hot press technique was carried out by applying heat at 100 °C, 160 °C and 180 °C for 30 minutes. The nanocomposite membranes were characterized by field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectrometry (EDX), differential scanning calorimetry and UV-vis-near-infrared spectroscopy. The FESEM images and EDX analysis showed good adhesion and dispersion of TiO₂ nanofibers in the PVDF membrane. Nanocomposite membrane prepared at hot pressing temperature of 100 °C (PVDF/e-TiO₂-100) exhibited appropriate morphological structure and physical properties. PVDF/e-TiO₂-100 exhibited the highest photocatalytic activity in the degradation of bisphenol A (BPA) under UV irradiation compared to the PVDF/e-TiO₂-160 and PVDF/e-TiO₂-180 with degradation rate of 84.53 %, 77.61 % and 62.54 %, respectively. Meanwhile, the pure water flux was reduced as the hot press temperature increased; 15.79 L/m².h (100 °C), 14.80 L/m².h (160 °C), 8.88 L/m².h (180 °C). However, the BPA rejection of the PVDF/e-TiO₂-100 was found to be the lowest among the prepared nanocomposite membranes. Based on the obtained results, it can be concluded that a fine-tuning on the optimization study of the membrane pore size by several approaches is required in order to ensure the developed PVDF/e-TiO₂ membranes can be efficiently functioned by means of photodegradation and filtration applications.

ABSTRAK

Pengoksidaan fotopemangkinan pada masa kini telah menjadi proses yang berharga untuk pembersihan air dan udara disebabkan oleh keupayaannya untuk mendegradasi pencemar organik. Fotodegradasi bahan pencemar organik oleh ampaian fotomangkin mempunyai kelemahan utama daripada segi kesukaran untuk merawatnya selepas digunakan. Dalam kajian ini, membran komposit nano polivinilidena florida (PVDF) yang terdiri daripada gentian nano pintalan elektro nanogentian titanium dioksida (TiO_2) (PVDF/e- TiO_2) telah disediakan melalui proses tekanan panas gentian nano TiO_2 di atas membran kepingan rata PVDF. Gentian nano TiO_2 bertindak sebagai fotomangkin, manakala membran PVDF bertindak sebagai sokongan. Teknik tekanan panas telah dijalankan pada suhu 100 °C, 160 °C dan 180 °C selama 30 minit. Membran komposit nano telah dianalisa dengan mikroskopi medan pengimbas elektron (FESEM), spektroskopi serakan tenaga sinar x (EDX), kalorimeter pengimbasan pembezaan, dan spektroskopi UV-vis inframerah terhampir. Imej FESEM dan analisis EDX menunjukkan lekatan dan taburan gentian nano TiO_2 yang baik dalam membran PVDF. Penyediaan membran komposit nano pada suhu 100 °C mempamerkan struktur morfologi dan ciri-ciri fizikal yang bersesuaian dengan aplikasi. PVDF/e- TiO_2 -100 mempamerkan aktiviti fotopemangkinan tertinggi dalam degradasi bisfenol A (BPA) di bawah sinaran UV berbanding PVDF/e- TiO_2 -160 dan PVDF/e- TiO_2 -180. Peratusan degradasi masing-masing adalah 84.53 %, 77.61 % dan 62.54 %. Fluks air tulen telah berkurangan apabila suhu tekanan panas meningkat; 15.79 L/m².h (100 °C), 14.80 L/m².h (160 °C), 8.88 L/m².h (180 °C). Walau bagaimanapun, PVDF/e- TiO_2 -100 didapati menyingkirkan BPA paling rendah di antara membran komposit nano PVDF/e- TiO_2 yang lain. Berdasarkan keputusan yang diperolehi, dapat disimpulkan bahawa kajian pengoptimuman terhadap saiz liang membran dan struktur membran komposit nano adalah penting bagi memastikan membran PVDF/e- TiO_2 berfungsi dengan cekap semasa aplikasi fotodegradasi serta aplikasi pemisahan.

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LIST OF ABBREVIATIONS

AOP	-	Advanced Oxidation process
BPA	-	Bisphenol A
BSA	-	Bovine Serum Albumin
EDC	-	Endocrine Disrupting Compound
DSC	-	Differential Scanning Calorimetry
FESEM	-	Field Electron Scanning Microscopy
FTIR	-	Fourier Transform Infrared
HPLC	-	High Performance Liquid Chromatography
MF	-	Microfiltration
NF	-	Nanofiltration
PAN	-	Polyacrylonitrile
PE	-	Polyethylene
PMR	-	Photocatalytic Membrane Reactor
PS	-	Polysulfone
PTFE	-	Polytetrafluoroethylene
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
PWF	-	Pure Water Flux
RO	-	Reverse Osmosis
TiO ₂	-	Titanium Dioxide
TNF	-	Titanium Dioxide Nanofibers
TTIP	-	Titanium Tetraisopropoxide
UF	-	Ultrafiltration
UV	-	Ultraviolet
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

A	-	Effective membrane area, m^2
C_0	-	Initial concentration of pollutants, ppm
C_t	-	Concentration of pollutants at time, ppm
c_f	-	Pollutants concentration in the feed, ppm
c_p	-	Pollutants concentration in the permeate, ppm
E_g	-	Band gap energy, eV
$h\nu$	-	Photon energy, eV
J	-	Pure water flux, $L/m^2.h$
l	-	Membrane thickness, m
Q	-	Permeate water volume over time, $m^3.s^{-1}$
r_m	-	Membrane mean pore size, nm
W_d	-	Weight of dry membrane, g
W_w	-	Weight of wet membrane, g
v	-	Permeate water volume, L
Δt	-	Time of the permeate collection, h
ΔP	-	Load pressure, Pa
ε	-	Membrane porosity, %
ρ	-	Density of water, 0.998 g/cm^3
η	-	Water viscosity, $8.9 \times 10^{-4}\text{ Pa.s}$
λ	-	Wavelength, nm

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Increasing demands and shortage of clean water sources due to the rapid development of industrialization, population growth, and long-term drought have become a serious issue worldwide. Due to this problem, various practical strategies and solutions have been adopted to yield more viable water resources. Wastewater is liquid waste discharged by domestic residences, commercial properties, industries, and agricultural activities, which often contain some contaminants resulting from the mixing of wastewater from different sources (Busca *et al.*, 2008). However, it is worth to realize that wastewater also consists of pure water, and therefore numerous processes have been implemented to clean up waste water depending on the type and extent of contamination (Teh and Mohamed, 2011). Disposal untreated waste water or minimal wastewater treatment of household and factories directly into drains and rivers has resulted in contaminated raw surface water (Musson and Townsend, 2009). Treated wastewater then can be reused as drinking water after it has been cleared from contaminants. The treatment of wastewater is not only important for health, but also to environment. Without proper treatment, many ecosystems would be severely damaged once the treated water is discharged into the environment.

Currently, there are several conventional wastewater treatments available in order to treat specific wastes such as sewage, industrial and agricultural wastes, and radioactive wastewater. There is no treatment technology that applies the same to all

pollutants removal. Among those wastewater treatments, membrane technology is leading in providing promising and innovation approach in upgrading and expansion of wastewater treatment plant (Madaeni *et al.*, 2011). This technology can improve the purification of the wastewater, make it more attractive compared to the conventional methods (Singh *et al.*, 2008). Membrane technologies are looking forward to increase the effectiveness of treating pollutants in wastewater treatment, however it also possessed some limitations related to fouling that will consequently reduce the permeate flux and efficiencies of the separation process (Shon *et al.*, 2007). Photodegradation of pollutants in wastewater via the application of photocatalysis is compromising as the best technology in treating micro pollutants and to reduce membrane fouling problems.

Wastewater from pharmaceutical industries poses one of the biggest challenges to the industrial waste treatment system. A wide variety of products in the pharmaceutical manufacturing industries require large amount of chemical substances in the manufacturing process. Waste water streams generated from this pharmaceutical manufacturing have been heavily contaminated with different type of chemicals, toxins and organic contents. Along with very complex contaminants, it becomes challenging for the treatment of the wastewater as the regulations for waste discharged is very stringent. Endocrine-disrupting compound (EDC) is one of the pharmaceutical wastes that require a critical concern for its treatment. For years, EDC have been detected in wastewater effluents and raw drinking water sources around the world at very low concentrations (Yoon *et al.*, 2007). Since EDC have potential risk to humans and wildlife even at the minimal trace levels, removal of EDC becomes important in water industry in order to protect the environment and eliminate refractory organic.

Nowadays, photocatalytic process has shown a great potential as a low-cost, and sustainable treatment technology in wastewater industry. The ability of this advanced technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. Recently, the main technical barriers that impede its commercialization remained on the post-recovery of the catalyst particles after the water treatment. To date, the photocatalyst recovery can be achieved by the

hybridization of the catalyst onto the support materials. Although the immobilization of the photocatalyst on the support materials will reduce the amount of catalyst active site, it can reduce the catalyst post-recovery step and at the same time can reduce the cost of the process.

Over the last decades, a great deal of interest has been focused on the photodegradation of organic compounds presence in water and wastewaters with the application of Titanium dioxide (TiO_2) as the photocatalyst. Generally, TiO_2 has been considered as one of the best semiconductor photocatalysts available for photocatalysis, due to its high photoactivity and photodurability owing to chemical and biological inertness, mechanical robustness, flexibility in its surface function, high mechanical stability, large surface area to volume ratio towards the light irradiation, and low cost (Doh *et al.*, 2008). The vast surface area of nanostructured TiO_2 photocatalyst allows high in excellent interaction between the pollutants and the catalyst, leading to better photocatalytic activity (Herrmann, 1999). Nanoparticles, nanotubes, nanowires, nanorods, and nanofibers are several forms of nanostructured photocatalysts that were produced for their higher purity, large surface area, and great size uniformity. These fascinating properties have an ability to reduce the toxicity of the pollutants to a safer level at reasonable cost (Colmenares *et al.*, 2009).

Photodegradation of organic pollutants by suspended photocatalyst has a major drawback in terms of difficulty to separate very small particles of the photocatalyst which requires another post-recovery treatment. To overcome this difficulty, the immobilizations of photocatalyst in/on a support/host have been introduced. Nowadays, membrane support has been widely used for photocatalyst in photocatalytic process. However, the incorporation of the photocatalyst in/onto the polymeric membrane support results in a loss of photoactivity, attributed by the reduced active surface accessible for components of the solution. It is believed that, the immobilization of the photocatalyst in/on the membrane support can be improved by introducing nanomaterials. In addition, the optimization study of the membrane microstructures and characteristics by several approaches is necessary to develop photocatalytic membranes with enhanced photocatalytic properties.

1.2 Problem Statement

Disposal untreated waste water or minimal wastewater treatment of household and factories directly to drains and rivers has resulted in contaminated raw surface water. With the deterioration in water quality, the use of clean water for daily use such as cooking, washing clothes, cleaning the dirt, to drink and so on is impaired. There are many contaminants or a pollutant that can caused disease that is depends on the type of pollutants that present in the wastewater itself. High pressure-driven membranes such as nanofiltration (NF) or reverse osmosis (RO) might be a powerful option to deal with such micro-pollutants (Kimura *et al.*, 2004). However, lack of information on their performance is apparent. Among various types of organic micro-pollutants with low molecular weight, endocrine disrupting compounds (EDCs) have been received a considerable attention recently. With rapid development of analytical techniques, it has been reported even at very low concentration, EDC effluents have become a major source of pollutant that polluted many aquatic environments. Pollution of drinking water sources with organic micro-pollutants is one of the great concerns in such situations. Their concentrations in the raw water were affected by the percentage of treated wastewater. One of EDCs that available abundantly in wastewater is bisphenol A (BPA). For instance, BPA is an important raw material in the production of polycarbonate plastics and epoxy resins, which high volume of this chemical waste produced daily could severely affect the aquatic ecosystem, as well as human.

To overcome this problem, the use of membrane filtration processes has been widely utilized over the past decade in order to remove the unwanted micro- and macro- particles. For example, unwanted particles that attached the outer layer of membrane thus forming a cake layer became the main obstacle in membrane filtration efficiency as it affected the productivity (Leong *et al.*, 2014). This phenomenon has practically and economically retarded membrane applications in water treatment development. The reduction in productivity caused by membrane fouling can be interpreted as the declined in flux with time of operation due to the increased of hydraulic resistance. It also can be defined that extra energy supply is needed by the membrane filtration system in order to maintain the system

performance. Moreover, the cleaning processes have been introduced to the system to remove the cake layer from the outer layer of membrane so that it can produce the permeate volume as much as at earlier stages.

At the moment, photocatalytic oxidation has been pledging as the valuable process for air and water purification because of its capability to produce harmless products by degrading the organic pollutants without the involvement of chemicals (Huang *et al.*, 2007; Litter, 1999). This advanced oxidation process (AOPs) has a variety of reactions such as organic synthesis, water splitting, photo reduction, hydrogen transfer, gaseous pollutant removal, and others (Gaya and Abdullah, 2008; Herrmann, 1999). The photocatalytic process has a great deal of interest in photodegradation of organic compounds present in wastewater with incorporation of titanium dioxide (TiO_2) as a photocatalyst.

Over the past decades, nanomaterials show a wide ranging potential in various major areas including industrial, biomedical and electronic applications. It has attracted the attention of many people especially researcher to further research and to improve the characteristics of the nanomaterials. Nanomaterial such as nanoparticles (Fischer *et al.*, 2015), nanowires (Zhang *et al.*, 2015), nanofibers (Vahtrus *et al.*, 2015), and nanotubes (Arruda *et al.*, 2015) only have size ranging from 1-100 nm. Commonly, nanomaterial is used as a catalyst in order to improve the process efficiencies because of the small particles will lead to a greater surface area for the reaction between pollutants and catalyst (Shen *et al.*, 2014). Due to its high active surface area, nanomaterial can be used to reduce the toxicity of pollutants to safer level at very reasonable cost (Kriklavova and Lederer, 2011). Nanofibers membrane is one of the advanced technologies used because of its small pore size and large surface area to volume ratio. It also has a good flexibility of its surface function and high mechanical performance such as tensile strength (Huang *et al.*, 2003; Lev *et al.*, 2011). The excellent features of nanofibers lead to many important technology development applications.

There are several techniques have been used to produce nanofibers such as melt blowing, forcespinning, and electrospinning. For example, heated air blows

were used to produce nanofibers in melt blown process while in forcespinning, the centrifugal forces has been used to turn the material into nanofibers (Ellison *et al.*, 2007; Padron *et al.*, 2013). Apart from that, electrospinning is the simplest available method used to produce fibers with diameters ranging between 10nm to 10 μm by accelerating a jet of charged precursor solution in an electric field (Nor *et al.*, 2013; Vonch *et al.*, 2007).

The suspended TiO_2 photocatalysts have higher photocatalytic efficiencies because the overall active surface of the TiO_2 particles are in contact with the organic pollutants in water/air and directly absorbed more UV light. However, this kind of process requires another post-treatment in order to separate the catalyst which are the discharge of the catalyst with effluent might be harmful to the ecosystem due to its biological accumulative effect (Grieken *et al.*, 2009). To overcome these problems, the immobilized TiO_2 catalyst on the support material has been introduced. Compared to the suspended applications, the immobilized TiO_2 photocatalyst on the support requires only one-step process. This kind of configuration exhibits a major drawback such as low photocatalytic activity due to the less active surface area of the attachment of the TiO_2 catalyst on the support (Gao and Liu, 2005).

There are several methods can be used to immobilize the TiO_2 photocatalyst on the membrane support (Chong *et al.*, 2010). Dip coating or spinning, blending, hot pressing, and physical or chemical cross-linking are some of the methods incorporating hybrid membrane (Bonchio *et al.*, 2006; Mohamed *et al.*, 2015a; Okur *et al.*, 2013; Romanos *et al.*, 2013). In several studies, hot pressing methods were done by applying both pressure and heat to improve the connectivity between fiber and membrane intersection (Lu *et al.*, 2002; Yuliwati *et al.*, 2011). Membrane compactness, mechanical properties and chemical stabilities of membrane will be improved by applying the concurrent application of pressure and heat (Na *et al.*, 2009). The losses strands of the nanofibers that are present on the top of the surface would also be eliminated as reported by Na *et al.* (2009) who studied the effect of hot press treatment on the electrospun PVDF membrane.

The current conventional methods used for wastewater treatment incapable for treating micropollutants such as EDCs and this might due to the compounds complexity and persistence. There is no such technology approach or treatment method that applies the same to all EDCs removal. Due to its high surface area, nanofibers have been used in this technique as it can enhance the filtration efficiency. Therefore, the current research was conducted to explore the possibility and effectiveness of EDCs removal in wastewater by using nanofiber coating on the membrane for membrane separation and photodegradation applications.

1.3 Objective of Study

The aim of this study is to investigate the removal efficiency of Bisphenol A (BPA) via photocatalytic process using the developed hybrid membrane made of PVDF-based membrane coated with TiO_2 nanofibers. The specific objectives of this study are:

- 1) To study the effect of TiO_2 precursor solution concentrations on the physical properties of TiO_2 nanofibers
- 2) To study the effects of hot pressing temperature on morphological structure of TiO_2 nanofibers coated onto PVDF membrane
- 3) To investigate the photocatalytic performances and membrane separation properties of flat sheet PVDF/e-spun TiO_2 nanocomposite membrane towards BPA removals

1.4 Scope of Study

In order to achieve the above mentioned objectives, the following scopes are outlined:

- 1) Preparing TiO_2 precursor solution by varying the concentration of (0.5g, 1.0g and 1.5g) polyvinylpyrrolidone, PVP in 1.6mL of titanium tetraisopropoxide (TTIP) under electrospinning process.
- 2) Analysing the morphological structure and the diameter of the resultant TiO_2 nanofibers using scanning electron microscope (SEM).
- 3) Preparing the polyvinylidene fluoride (PVDF) flat sheet membrane using phase inversion technique as a nanocomposite membrane support.
- 4) Developing the coating process of PVDF membrane with as-spun TiO_2 nanofibers using hot press method at temperature of 100°C , 160°C and 180°C for 30 minutes.
- 5) Characterizing the PVDF/e-spun TiO_2 nanofibers in terms of morphological structures and structural properties towards photocatalytic process by using field electron scanning electron microscope (FESEM), energy dispersive X-ray analysis (EDX), thermal properties by differential scanning calorimetry (DSC) and optical absorption behaviour by ultraviolet-visible-near-infrared spectrophotometry (UV-VIS-NIR).
- 6) Investigating the photocatalytic performance of the prepared PVDF/e-spun TiO_2 nanofibers for the photodegradation of BPA by using high performance liquid chromatography (HPLC) coupled with a programmable UV detector.

- 7) Examining the performance of the PVDF/e-spun TiO_2 nanofibers toward membrane separation through the membrane physical characteristics in terms of membrane hydrophilicity, pure water flux, membrane porosity, membrane mean pore size, and membrane rejection.

1.5 Significance of Study

In recent years, membrane based photocatalytic technology was nominated as an Advanced Oxidation Process (AOP) owing to its promising ability to degrade trace level environmental pollutants via hybrid technology approach such as photodegradation and membrane separation. The utilization of TiO_2 nanofibers as the photocatalyst was found to be interesting due to the flexibility in its surface function, high mechanical stability, and very large surface area to volume ratio towards the light irradiation. These properties are significantly meaningful for a maximum light absorption and simultaneously improved the photocatalytic activity. Furthermore, the immobilization of TiO_2 nanofibers on the PVDF membrane support can simplify the conventional photocatalytic process by eliminating the post treatment of catalyst separation process. The significant improvement in this study, indicated that the photocatalytic membrane is vital to sustain a clean and safer environment.

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